



Review

Global emission inventories for C₄–C₁₄ perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources



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ABSTRACT

We quantify global emissions of C₄–C₁₄ perfluoroalkyl carboxylic acid (PFCA) homologues during the life-cycle of products based on perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctane sulfonyl fluoride (POSF), and fluorotelomer compounds. We estimate emissions of 2610–21400 tonnes of C₄–C₁₄ PFCAs in the period from 1951 to 2015, and project 20–6420 tonnes to be emitted from 2016 to 2030. The global annual emissions steadily increased in the period 1951–2002, followed by a decrease and then another increase in the period 2002–2012. Releases from fluoropolymer production contributed most to historical PFCA emissions (e.g. 55–83% in 1951–2002). Since 2002, there has been a geographical shift of industrial sources (particularly fluoropolymer production sites) from North America, Europe and Japan to emerging Asian economies, especially China. Sources differ between PFCA homologues, sometimes considerably, and the relative contributions of each source change over time. For example, whereas 98–100% of historical (1951–2002) PFOA emissions are attributed to direct releases during the life-cycle of products containing PFOA as ingredients or impurities, a much higher historical contribution from PFCA precursor degradation is estimated for some other homologues (e.g. 9–78% for PFDA). We address the uncertainties of the PFCA emissions by defining a lower and a higher emission scenario, which differ by approximately a factor of eight.

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Terminology

1. The emission inventory of C_4 – C_{14} perfluoroalkyl carboxylic acid (PFCA) homologues is arranged by investigating the fate of certain chemical species during the life-cycle of relevant products. The products are grouped and named after the major ingredients therein, e.g. products containing perfluorooctanoic acid (PFOA) and its derivatives that have the same functional moiety (i.e. the perfluoroalkane carbonyl moiety, $C_nF_{2n+1}C(O)-$; including salts, esters, etc.; hereafter *derivatives* only) as major ingredients are categorized as PFOA-based products. The same terminology is used for other products, including fluorotelomer-based products and products based on perfluorononanoic acid (PFNA) and perfluorooctane sulfonyl fluoride (POSF). In addition to those species that are intentional ingredients in products, [i] PFCAs and their derivatives present in products as undesired byproducts (hereafter *impurities*) and [ii] POSF- and fluorotelomer-based substances present in products as unreacted raw materials (hereafter *residuals*) are also accounted for in the inventory.
2. PFCA sources are divided into two categories. *Direct* sources include PFCA emissions from the life-cycle of [i] PFCA-based products that contain PFCAs or their derivatives as major ingredients and [ii] other products in which PFCAs and/or PFCA derivatives are present as impurities. *Indirect* sources refer to formation of PFCAs from degradation of precursors such as POSF- and fluorotelomer-based substances in the environment and biota. For details and examples of POSF- and fluorotelomer-based precursors of PFCAs, see Frömel and Knepper (2010), Liu and Avendaño (2013), Young and Mabury (2010), and the references therein. In this work we adopt the terminology proposed by Buck et al. (2011), which is slightly different from that used by Prevedouros et al. (2006), regarding whether PFCA impurities in other products are considered as direct (here) or indirect sources (by Prevedouros et al., 2006). Details on terminology are provided in *Section S0* in the *Supplementary Data*.
3. PFCAs and their POSF- and fluorotelomer-based precursors belong to the chemical class known as poly- and perfluorinated alkyl substances (PFASs). PFASs are chemicals that contain one or more perfluoroalkyl moieties, $-C_nF_{2n+1}$ (Buck et al., 2011). In the past, PFASs were often referred to as “PFCs” (per- and polyfluorinated chemicals), but this acronym is also commonly used for perfluorocarbons; perfluorocarbons contain only carbon and fluorine and have properties and functionalities different from those of PFASs.

1. Introduction

Long-chain perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $n \geq 7$), including perfluorooctanoic acid (PFOA or C_8 PFCA) and perfluorononanoic acid (PFNA or C_9 PFCA), are recognized as global contaminants of high concern, since they are highly persistent (Frömel and Knepper, 2010; Parsons et al., 2008; Young and Mabury, 2010), bioaccumulative (Conder et al., 2008; ECHA, 2013), and have been detected globally in the abiotic environment (Rayne and Forest, 2009), biota (Giesy and Kannan, 2001), food items (Picó et al., 2011) and humans (Vestergren and Cousins, 2009). In the European Union (EU), C_{11} – C_{14} PFCAs are identified as very persistent and very bioaccumulative (vPvB) substances and PFOA and its ammonium salt (APFO) are identified as persistent, bioaccumulative and toxic (PBT) substances (ECHA, 2013). These PFCA homologues have therefore been added to the Candidate List of Substances of Very High Concern (SVHCs) for Authorisation under the European Chemical Regulation, REACH (EG 1907/2006) (ECHA, 2013).

In order to characterize human and environmental exposure to PFCAs, it is important to understand their levels and trends in the environment, starting with source identification and quantification. Only fragmented information was available until Prevedouros et al. (2006) compiled available information and estimated the total global historical emissions of PFCAs (1951–2004) during the life-cycle of fluorotelomer-based products and products based on PFOA, PFNA and perfluorooctane sulfonyl fluoride (POSF). General information on the production, major uses and relevance to PFCA emissions of these four product groups is compiled in Fig. 1; for details on each product group, see *Section S1* in the *Supplementary Data*. The work by Prevedouros et al. (2006) highlighted the significance of historical direct sources to the overall presence of PFCAs in the environment, in particular from production of certain fluoropolymers where PFOA- or PFNA-based products have been used as processing aids (Prevedouros et al., 2006). Prior to Prevedouros et al. (2006), indirect sources, in particular atmospheric degradation of residuals in POSF- and fluorotelomer-based products,

had been postulated to be the major source of PFCAs in the environment (Ellis et al., 2004). Precursor degradation may well be the dominant source of PFCAs in remote inland environments such as the high Arctic or alpine lakes that are impacted only by atmospheric inputs (Benskin et al., 2011; Schenker et al., 2008; Young et al., 2007), but indirect sources are probably not dominant for other environments (e.g. open oceans) or the globe as a whole (Armitage et al., 2006, 2009a,b).

The availability of emission data made it possible to employ environmental fate models in order to elucidate the global fate of PFCAs and, in particular, their transport pathways to remote areas (Armitage et al., 2006, 2009a,b; Schenker et al., 2008; Stemmler and Lammel, 2010; Wania, 2007). These modeling studies were recently reviewed (Cousins et al., 2011) and were found to support the notion that direct uses of PFOA- and PFNA-based derivatives as processing aids in certain fluoropolymer production are the dominant historical global sources for these PFCA homologues (Prevedouros et al., 2006). The same review also concluded that PFCA homologue patterns in monitoring data indicate that *indirect* sources may become proportionally more important for PFCA homologues with nine or more perfluoroalkyl carbons (Cousins et al., 2011). Hence, the major sources of other PFCA homologues may differ from those of PFOA and PFNA, and need to be assessed individually. However, Prevedouros et al. focused mainly on PFOA and PFNA; a detailed breakdown of PFCA emissions on a homologue basis was not provided (Prevedouros et al., 2006).

When historical PFCA emissions are characterized, it is important to account for changes in industrial practices of PFASs that have occurred over time. There has been a trend amongst global producers to replace chemicals containing long perfluoroalkyl chains (e.g. PFCAs with ≥ 7 perfluoroalkyl carbons or perfluoroalkane sulfonic acids with ≥ 6 perfluoroalkyl carbons as defined by OECD; Buck et al., 2011) with their shorter-chain homologues (Ritter, 2010; Wang et al., 2013) or with other fluorinated and non-fluorinated substances (Buck et al., 2011; Wang et al., 2013). These industry initiatives began in 2000 when 3M announced a global phase-out of its products based on C_6 , C_8 and C_{10} perfluoroalkane sulfonyl fluoride (PASf)-based chemistry

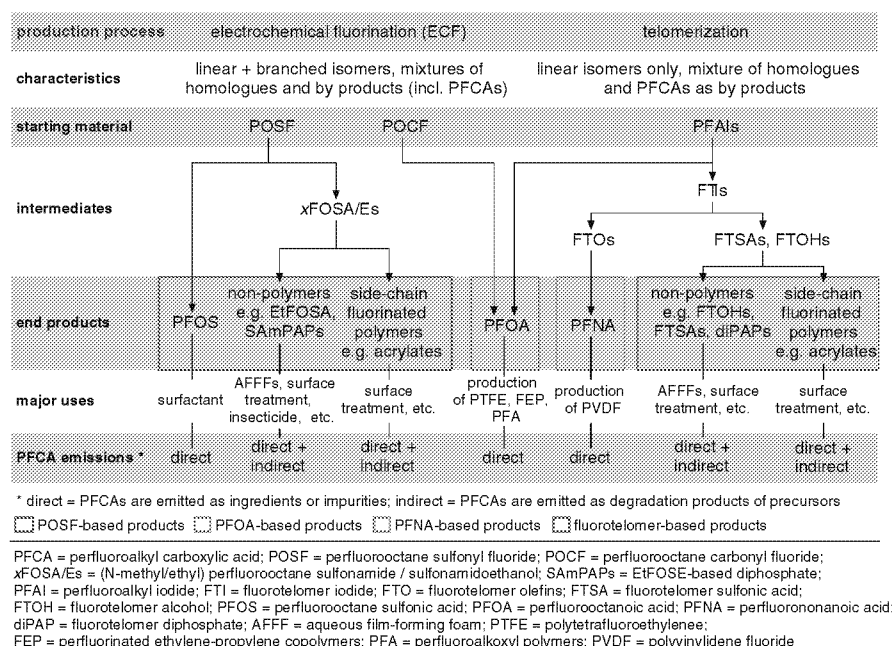


Fig. 1. General information on the production and uses of perfluorooctanoic acid (PFOA)-, perfluorononanoic acid (PFNA)-, perfluorooctane sulfonyl fluoride (POSF)- and fluorotelomer-based products as well as their relevance to the emissions of C_4 – C_{14} PFCAs.

and replaced them with products based on C_4 chemistry such as perfluorobutane sulfonic acid (3M, 2000a; Ritter, 2010). In 2006, eight major PFOA, fluoropolymer and fluorotelomer manufacturers joined the global US EPA 2010/15 Stewardship Program (US EPA, 2006) to work toward the elimination of long-chain PFCAs and their precursors from emissions and products by 2015. While long-chain PFCAs and their precursors are being phased out in a series of steps by major producers in Japan, Western Europe and the United States (US) (US EPA, 2006), new producers (largely in continental Asia) have begun to produce long-chain PFCAs and their precursors (for details and references, see Section 3.3, *Analysis of industrial sources*). Thus, emission sources have changed since the review by Prevedouros et al. (2006) was published.

This study aims to re-evaluate and expand on the work presented by Prevedouros et al. (2006). To this end, an extensive literature research was conducted including all but not limited to the sources summarized in Prevedouros et al. (2006). As a result, a new, more comprehensive set of PFOA sources were identified and efforts were made to quantify emissions from as many sources as possible. Due to a lack of data (on production, use, and disposal, and in some cases also degradation half-lives and yields), not all sources can be quantified. Hence, we divide this study into two parts. In this paper, we focus on the sources that can be quantified, whereas information on those sources that are known to exist but can currently not be quantified is summarized and presented in a companion paper (Wang et al., 2014).

In the *Results* section, we present global emission estimates of C_4 – C_{14} PFOA homologues from the life-cycle of PFOA-, PFNA-, POSF- and fluorotelomer-based products in three periods (1951–2002, before the phase-out by 3M; 2003–2015, transition toward alternatives after the phase-out by 3M; 2016–2030, projection). In addition, we assess the geographical distribution of emissions from industrial sources and the receiving environmental media as a function of time with special attention to the macroeconomic trend of production moving to continental Asia. In the *Discussion* section, we evaluate our estimates by comparing them to (i) several studies that estimated POSF- and fluorotelomer-based precursor emissions with different methods, and (ii) estimated amounts of PFOA homologues in open ocean surface water derived from monitoring studies. Also, we discuss accuracy,

uncertainties and limitations of the emission estimates presented here and highlight areas where there are key uncertainties. It should be noted that our estimates (such as levels or homologue patterns) cannot be directly compared to measurements at a single site or source because they represent aggregated emissions from different sources on a global basis. Finally, the fate and behavior of PFOA homologues after being released into the environment (e.g., reactions with OH radicals; Hurley et al., 2004) is beyond the scope of this study and thus not included.

2. Methods

2.1. Identification of PFOA sources

We conducted an extensive literature review of over 4500 documents in the public domain, including peer-reviewed scientific articles, books, theses, monographs, conference abstracts, industrial studies, patents, as well as databases and technical reports from international bodies. In addition to the sources reviewed by Prevedouros et al. (2006) (i.e., emissions from PFOA-, PFNA-, POSF- and fluorotelomer-based products), we identified several other sources that (may) contribute to the presence of PFCAs in the environment (see Fig. 2, left). For most of the newly identified sources there is a general lack of information on [i] the production, use and disposal of relevant products and [ii] the degradation half-lives and yields (in the cases of indirect sources), preventing these sources from being quantified. Therefore, all identified sources were divided into two groups based on data availability. Quantifiable sources include PFOA-, PFNA-, POSF- and fluorotelomer-based products (see Fig. 2, right); for these sources the PFOA emissions were quantified as explained below and in the *Supplementary Data*. For the other sources, we reviewed available information and highlight the critical knowledge/data gaps in a companion paper (Wang et al., 2014).

2.2. Quantification through the product life-cycle

Due to limited space, here we only report the general approach; Section S1 in the *Supplementary Data* provides details on all parameters

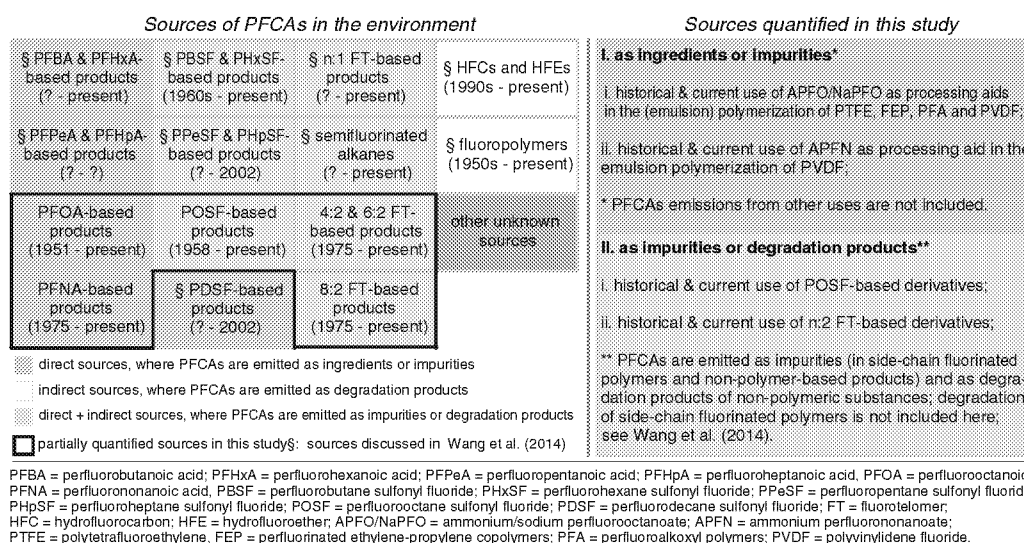


Fig. 2. Left: sources of perfluoroalkyl carboxylic acids (PFCAs) in the environment and their likely time span; right: sources quantified in this study.

(including data treatment and references). In general, we combined data (retrieved from our literature search) on products containing PFCAs and/or their precursors (including manufacturing processes, production volumes as a function of time, and use patterns) with estimated or empirically derived emission factors during each stage in the product life-cycle (see Fig. 3).

In comparison to Prevedouros et al. (2006), we updated parameters such as emission factors (see Tables S66 to S68 in the *Supplementary Data*) and also improved the quantification in the following six respects:

- Average life-cycle duration.** Instead of the earlier assumption that PFCA emissions occur in the year when a “source” substance is produced (Prevedouros et al., 2006), we assigned an average duration to each stage in the product life-cycle; this ranges from immediate (production and disposal phase) up to ten years (use phase; duration was set based on product type and use pattern (polymers vs. non-polymers); see Sections S1.1.1.5, S1.3.1.3.2 and S1.4.1.3.2 in the *Supplementary Data*). This improves the understanding of temporal trends in emissions during use and disposal of products, particularly for the post phase-out period.
- Two country groups.** In order to track the geographical shift of industrial sources, we conducted our estimation separately, wherever

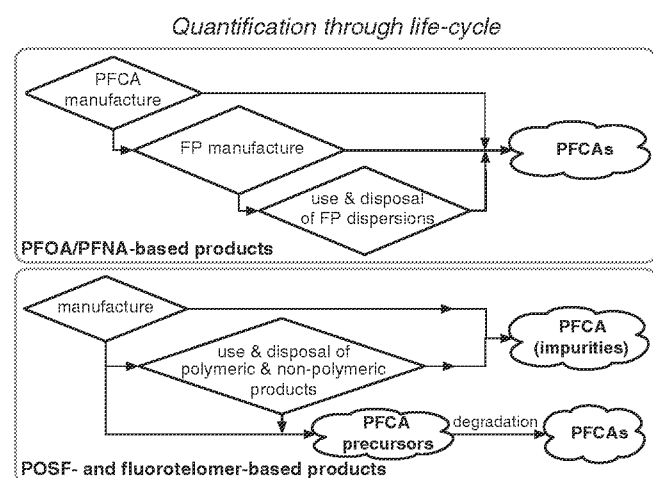


Fig. 3. Schematic diagram of PFCA emission quantification through the life-cycle of PFOA-, PFNA-, POSF- and fluorotelomer-based products. (FP = fluoropolymers).

possible, for two country groups: I (Japan, Western Europe and the US) and II (Russia, China, India and Poland).

- New estimates of PFCAs used in fluoropolymer production.** Due to limited information provided in the *Supporting Information* of Prevedouros et al. (2006), it was not possible to verify the previously reported amounts of relevant fluoropolymers produced and of PFOA- and PFNA-based products used as processing aids in fluoropolymer production. Hence, we estimated the amounts of PFOA- and PFNA-based derivatives used as fluoropolymer processing aids, based on [i] reported and estimated production volumes of relevant fluoropolymers (i.e., polytetrafluoroethylene or PTFE; perfluorinated ethylene-propylene copolymers or FEP; perfluoroalkoxy polymers or PFA; and polyvinylidene fluoride or PVDF) in country group I and II, and [ii] use rates of PFOA- and PFNA-based products in various fluoropolymer production processes documented in patents. Details of these new calculations are provided in Sections S1.1.1 and S1.2.1 in the *Supplementary Data*. Use rates of PFCAs as fluoropolymer processing aids in patents are often reported as wide ranges (for examples, see Tables S7 and S8 in the *Supplementary Data*). Therefore, one of the consequences of this new approach is that the estimated amounts of PFOA-based products applied have a wider range than in Prevedouros et al. (2006). Because there is little information on actual industrial practice in the literature, we decided not to arbitrarily narrow down the range of use rates, but to set an additional so-called “plausible” scenario. In this scenario, the use rate was set at 0.3 wt% of all relevant fluoropolymers produced, derived from [i] the APFO consumption in 1999 (ca. 200 tonnes) reported by the Fluoropolymer Manufacturers Group (FMG) (Pinchot, 2004) and [ii] the estimated production volume of relevant fluoropolymers by the FMG in 1999 (ca. 67 kt) (Kálin et al., 2012; Will et al., 2005). Thus, this use rate is likely close to the actual industrial practice and used as a reference value.

- Separation of non-polymeric and polymeric species.** A large proportion of POSF- and fluorotelomer-based PFCA precursors are chemically bound in side chains in so-called side-chain fluorinated polymers where the side chains are fluorinated but the backbone consists of non-fluorinated hydrocarbons, e.g., fluorinated (meth)acrylate polymers (Buck et al., 2011). The side chains of these fluorinated polymers are likely not readily degradable (i.e., not readily detached from the backbone) (Russell et al., 2008, 2010a,b; Washington et al., 2009, 2010). PFCA precursors present in non-polymeric form, in contrast, may be transformed into PFCA homologues within days

or weeks (Frömel and Knepper, 2010; Young and Mabury, 2010). Hence, we divided PFCA precursors into two groups, polymers and non-polymers. To do so, we introduced non-polymeric:polymeric ratios of different PFCA precursors and varied these ratios as a function of time (see Sections S1.3.1.3.1 and S1.4.1.3.1 in the *Supplementary Data*).

For non-polymeric species, we included not only residuals in products (e.g., surface-treated textiles or papers; Buck et al., 2011 and Martin et al., 2010) as in Prevedouros et al. (2006), but also species that were not included there, i.e. [i] substances with simple structures including N-ethyl perfluorooctane sulfonamide (EtFOSA) (Martin et al., 2010) or fluorotelomer sulfonic acids (FTSAs) (Buck et al., 2011; Lehmler, 2005) that are used as ingredients in products; and [ii] substances with complex structures such as phosphate diesters based on N-ethyl perfluorooctane sulfonamide ethanol (EtFOSE) [SAMPAps, e.g., $(C_8F_{17}SO_2N(C_2H_5)CH_2CH_2O)_2PO_2^-$] and their fluorotelomer-based analogues [diPAPs, e.g., $(C_8F_{17}CH_2CH_2O)_2-PO_2^-$] that can break down into substances such as EtFOSE or FTOHs through biodegradation in activated sludge (Lee et al., 2010) or sediment (Benskin et al., 2012a, 2013) and thus form a source of PFCA precursors (Schultz et al., 2006). This degradation behavior has also been observed for other substances, e.g. breakdown of 8:2 fluorotelomer stearate monoester (8:2 FTS, $C_8F_{17}C_2H_4OOC C_{17}H_{35}$) in soil (Dasu et al., 2010, 2012) and of 6:2 fluorotelomer sulfonamide alkylbetaine [6:2 FTAB, $C_6F_{13}C_2H_4SO_2NHC_3H_6N^+(CH_3)_2CH_2COO^-$] in biota or through photolysis (Moe et al., 2012). For degradation half-lives and yields, see Sections S1.3.3 and S1.4.3 in the *Supplementary Data*.

For polymeric species, due to large uncertainties associated with their degradation half-lives and yields, we did not account for polymer degradation, but did account for degradation of residuals (e.g., FTOHs or FOSEs) in products as in Prevedouros et al. (2006). In the companion paper, we investigate if degradation of these side-chain fluorinated polymers could be a relevant source of PFCAs (Wang et al., 2014).

- v PFCA emissions on a homologue basis. PFCAs, as ingredients or impurities, and their precursors are manufactured as homologue mixtures (Buck et al., 2011). To break down the PFCA emissions on a homologue basis, we associated total PFCA emissions with information on homologue compositions of PFCAs and/or PFCA precursors in commercial products. To fill data gaps, assumptions sometimes had to be made; assumed or estimated homologue compositions and explanations are provided in Tables S40, S46, S55, S56, S59, S61 and S62 in the *Supplementary Data*.
- vi Industrial transition period (2002–2015). Since 2002, major global producers of PFCAs, fluoropolymers and fluorotelomer-based products have implemented techniques to reduce industrial emissions as well as impurity and residual levels in products (US EPA, 2006), and have started to replace long-chain PFCAs and their precursors with shorter-chain homologues or other fluorinated and non-fluorinated substances (Buck et al., 2011; Ritter, 2010; Wang et al., 2013). In order to capture changes in PFCA emissions caused by these technological transitions, we incorporated information on the transition process (e.g., progress reports of the US EPA 2010/15 Stewardship Program; US EPA, 2006, 2008a,b, 2009a, 2010, 2011, 2012, 2013a) for the period 2002–2015 by [i] reducing the relevant emission factors (see Tables S29, S31, S35, S44, S45, S49 and S58 in the *Supplementary Data*); [ii] reducing the corresponding production volumes (see Tables S16, S22, S27, S43, S47 and S48 in the *Supplementary Data*); [iii] changing the homologue compositions (see Table S39, S51 and S59 in the *Supplementary Data*).

To project emissions in 2016–2030, we assumed that long-chain PFCAs and their precursors will no longer be produced in country group I based on the companies' commitment to the US EPA

Stewardship Program (US EPA, 2006), but may still be contained in products in these regions due to global trade. In contrast, only qualitative but no quantitative data on emission reductions are available for producers in country group II such as China (for details and references, see Section 3.3, *Analysis of industrial source* section). Hence, we set up two scenarios for producers in country group II: (i) a lower scenario in which producers cease production and use of long-chain PFCAs and their precursors in line with global transition trends and (ii) a higher scenario in which the emission scenario in 2015 is assumed to remain constant until 2030. For details, see Sections S1.1.1, S1.2.1, S1.3.1 and S1.4.1 in the *Supplementary Data*.

In order to evaluate our results, we compared our estimated emissions of PFCA precursors to air with three other studies that derived their estimates using different methods. Also, we compared our PFCA emission estimates to the inventory of PFCAs in open ocean water, which is the largest global reservoir of PFOA, PFNA and likely other PFCA homologues (Cousins et al., 2011). The ocean inventory was calculated by multiplying background levels of PFCAs in open ocean surface water (derived from monitoring studies) by the volume of the global ocean surface mixed layer (assuming 100–200 m depth with a median value of 150 m) (Armitage et al., 2009a; Prevedouros et al., 2006). Comparisons are presented in the *Discussion* section. For details, see Sections S2.4 and S2.5 in the *Supplementary Data*.

2.3. Analysis of industrial sources

In order to provide information on emission reduction potential, we developed profiles of the environmental media (air, water and land) receiving emissions and of the geographical distributions of industrial sources (including those industrial sites where PFOA-, PFNA-, POSF- and fluorotelomer-based products are manufactured and used as well as industrial waste treatment facilities). Each profile was derived from publicly accessible information on industrial sites (such as locations and on-site mass flows), technical expert knowledge, and our own estimates. In all cases, the mode of emission was assumed to be constant with time and homologue, whereas temporal changes were considered for geographical distributions. All profiles are provided in the *Supplementary Data* (see Section S2.2) and summarized in the *Results* section.

2.4. Uncertainty analysis

The methods in this study rest on various assumptions derived from limited empirical studies, which introduce uncertainties into the estimates. Using Monte Carlo simulation to quantify the uncertainties is currently not possible because for most of the parameters there is insufficient information on the range and/or distribution of their values. Instead, in those cases where the data were sufficient, parameters such as emission factors or levels of PFCA impurities in products were estimated in two scenarios (lower and higher) (Morgan, 2001; Refsgaard et al., 2007). Some other uncertainties introduced by using default values cannot be reliably quantified due to a lack of data. For instance, we might overestimate the amounts of PFCAs formed from precursors by using yields measured in laboratory experiments conducted with zero or low levels of NO_x (high levels of NO_x , especially in urban air, can lead to further degradation, shortening the perfluoroalkyl chain and ultimately leading to the formation of COF_2) (Young and Mabury, 2010). However, an adjustment factor to extrapolate data from laboratory studies to field conditions is not available. As there are different levels of uncertainties attributed to the various parameters, we introduced a scoring system to indicate for each parameter the level of uncertainty: 0–1 represents low uncertainty (reported estimates and/or measured emissions which have been evaluated for accuracy); 1–2 represents medium uncertainty (expert estimates or measured emissions which have not been (fully) evaluated); 2–3 represents high uncertainty (crude estimates or extrapolated emissions). Details

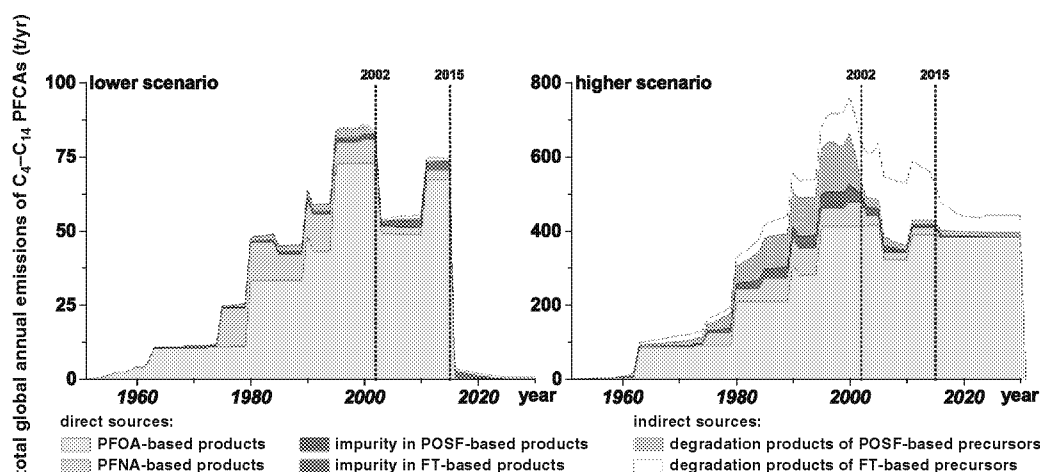


Fig. 4. Estimated total global annual emissions of C_4 – C_{14} PFCAs (1951–2030) from six quantified sources (left: lower scenario; right: higher scenario). PFOA – perfluorooctanoic acid; PFNA – perfluorononanoic acid; POSF – perfluorooctane sulfonyl fluoride; FT – fluorotelomer.

are provided in Section S3 in the *Supplementary Data* and summarized in the *Discussion* section.

3. Results

3.1. Estimated total global emissions of C_4 – C_{14} PFCAs from quantified sources

Fig. 4 and Table 1 display the estimated total global annual emissions and the cumulative global emissions of C_4 – C_{14} PFCAs from all quantified sources, respectively. The annual emissions show a steady increase in 1951–2002, followed by a decrease and then another increase between 2002 and 2012. This recent re-increase is caused by the industrial

transition in opposite directions in country groups I (decrease) and II (increase), which is elucidated in detail further below in Section 3.3. *Analysis of industrial sources.* After 2012, a further decline of PFCA emissions from industrial sites in country group I is expected based on the companies' commitments to the US EPA 2010/15 PFOA Stewardship Program (US EPA, 2006) and the on-going transition to replacements of long-chain PFCAs and their precursors (for details and examples, see Wang et al., 2013). Similar emission reduction actions by major producers in country group II have been reported, but in a rather qualitative manner with no clear timeline given (for details and references, see Section 3.3. *Analysis of industrial sources*). Therefore, it is likely that the emissions of long-chain PFCAs in country group II are being reduced and will be eliminated in the foreseeable future. However, due to a

Table 1

Estimated global cumulative emissions of total C_4 – C_{14} PFCAs from 1951 to 2030 in this study and from 1951 to 2002 in Prevedouros et al. (2006). Figures in brackets represent estimates based on a use rate of 0.3 wt% (of relevant fluoropolymers produced) PFOA-based products as processing aids in fluoropolymer production (i.e. the plausible scenario). FT = fluorotelomer.

Quantified emission source category		Prevedouros et al.		This study			
		1951–2002 [t]		1951–2002 [t]		2003–2015 [t]	
		Min.	Max.	Lower	Higher	Lower	Higher
Direct sources	<i>PFOA-based products</i>						
	1. PFOA manufacture	400–700		90 (200)	970 (570)	30 (90)	430 (280)
	2. Fluoropolymer (FP) manufacture with PFOA	2000–4000		1220 (2790)	6560 (3850)	660 (1700)	3870 (2430)
	3. Use & disposal of FP dispersions containing PFO	200–300		90 (210)	490 (290)	50 (140)	320 (200)
	<i>PFNA-based products</i>						
	4. PFNA manufacture	70–200		20	180	0	50
	5. PVDF manufacture with PFNA	400–1400		270	1270	30	220
	6. Use & disposal of PVDF dispersions containing PFN	10–20		10	20	0	0
	<i>POSF-based products, as impurities</i>						
	7. Manufacturing phase	20–130 ^b		1	30	0	0.1
Indirect sources	8. Use & disposal phase			12	746	1.5	101
	<i>FT-based products, as impurities</i>						
	9. Manufacturing phase	0.3–30 ^b		0	0	0	0
	10. Use & disposal phase			17	34	30	61
	<i>Degradation of POSF-based products</i>						
	11. Manufacture, use & disposal	1–30		50	2400	6	226
	<i>Degradation of FT-based products</i>						
	12. Manufacture, use & disposal	6–130		9	1518	13	1902
	Total direct sources ^c	3200–6900		1730 (3530)	10300 (6990)	800 (1990)	5050 (3340)
	Total indirect sources ^c	30–350		60	3920	20	2130
	Total emissions (direct + indirect) ^c	3200–7300		1790 (3590)	14220 (10910)	820 (2010)	7180 (5470)

^a Two scenarios for country group II were set up: (i) a lower scenario in which producers cease production and use of long-chain PFCAs and their precursors in line with global transition trends and (ii) a higher scenario in which the emissions in 2015 are assumed to remain constant until 2030.

^b The emission estimates in Prevedouros et al. (2006) include emissions both from manufacture and from use and disposal.

^c The figures are rounded to the nearest 10.

lack of quantitative data, it is unclear how rapidly emissions will be discontinued. In total, we estimate that 2610–21400 tonnes of C_4 – C_{14} PFCAs are emitted globally from 1951 to 2015 and project 20–6420 tonnes to be emitted from 2016 to 2030. Releases during the life-cycle of PFOA- and PFNA-based products contribute most to the emissions of C_4 – C_{14} PFCAs before 2015. Thereafter, the potential contributions from possible continuing production and use of PFOA-based products in certain fluoropolymer production in China and Russia as well as degradation of fluorotelomer-based substances are estimated to be the dominant emissions.

In Table 1, we compare our estimates of the total historical releases of PFCAs from 1951 to 2002 to the estimates by Prevedouros et al. (2006). In most cases, both estimates for total PFCa emissions agree well, particularly when the plausible scenario (i.e. assuming a use rate of 0.3 wt% PFOA-based products in fluoropolymer production) is used. A notable difference is that we obtain much higher PFCa emissions from the life-cycle of POSF- and fluorotelomer-based products, as impurities or degradation products. The causes of these higher estimates are elucidated in the Discussion section.

3.2. Estimated global emissions of individual homologues from quantified sources

Fig. 5 shows the relative contribution of each source to the total estimated global emissions of individual PFCa homologues from all quantified sources in two periods (1951–2002 and 2003–2015). The dominant sources differ (sometimes considerably) between PFCa homologues. In 1951–2002, PFCa homologues can be divided into three groups: (i) the majority of C_8 , C_9 , C_{11} and C_{13} PFCAs were emitted from PFOA- and PFNA-based products, (ii) >50% of the C_5 – C_7 PFCAs were released to the environment as degradation products of POSF- and fluorotelomer-based precursors, and (iii) for C_4 , C_{10} , C_{12} and C_{14} PFCAs, the dominant source differs in the lower and higher scenarios. Moreover, the relative contribution of each source changes over time. After 2002, emissions from PFOA- and PFNA-based products are less relevant than before for almost all PFCa homologues, whereas emissions from fluorotelomer-based products, as impurities or as degradation

products, are the dominant sources for most of the PFCa homologues after 2002.

Table 2 lists the estimated global cumulative emissions of individual PFCa homologues from all quantified sources in 1951–2002, 2003–2015 and 2016–2030. C_8 and C_9 PFCAs are the homologues released in largest amounts, followed by C_4 and C_5 PFCAs. PFCAs with ten or more carbons are emitted in relatively low amounts compared to other homologues.

3.3. Analysis of industrial sources

As shown in Table 1, most of the historical PFCa emissions from quantified sources occurred at industrial point sources where PFCa-based products were produced, used, or disposed of (sources 1, 2, 4 and 5 in Table 1). Here we take a closer look at these industrial sites, focusing on the mode of entry into the environment of emissions and on their geographical distribution (illustrated for PFOA-based products in Fig. 6), so as to provide information for future emission prevention or reduction measures. Major industrial events regarding PFCa, POSF- and fluorotelomer-based products that have likely resulted in increases or decreases in PFCa emissions since the 1950s are summarized in a timeline (see Figure S9 in the Supplementary Data).

Among all PFAS-related industrial sites, production sites of PFOA-based products and fluoropolymer production sites where PFOA-based products were used as processing aids are best studied. At these sites, most of the emissions occurred with wastewater streams, whereas small amounts were emitted with exhaust gases or solid wastes (see pie charts in Fig. 6). Since PFNA and its derivatives have physicochemical properties similar to those of PFOA and its derivatives, it is expected that a similar mode of entry occurred at sites where PFNA-based products were produced or processed. This is consistent with recent observations of high PFNA levels in industrial effluents from a metal-plating factory (US EPA, 2009b) and a textile factory (Clara et al., 2008). For POSF- and fluorotelomer-based derivatives, in contrast, a generalized mode of entry of emissions from industrial sites cannot be determined, because (i) at the primary production sites studied, only selected (but not all) substances were monitored in one or more (but not all) environmental compartments (3M, 2000b,c,d,e,f,g,h,i; Dauchy et al., 2012; Ruan et al., 2010) (ii) no mass flow study is yet available

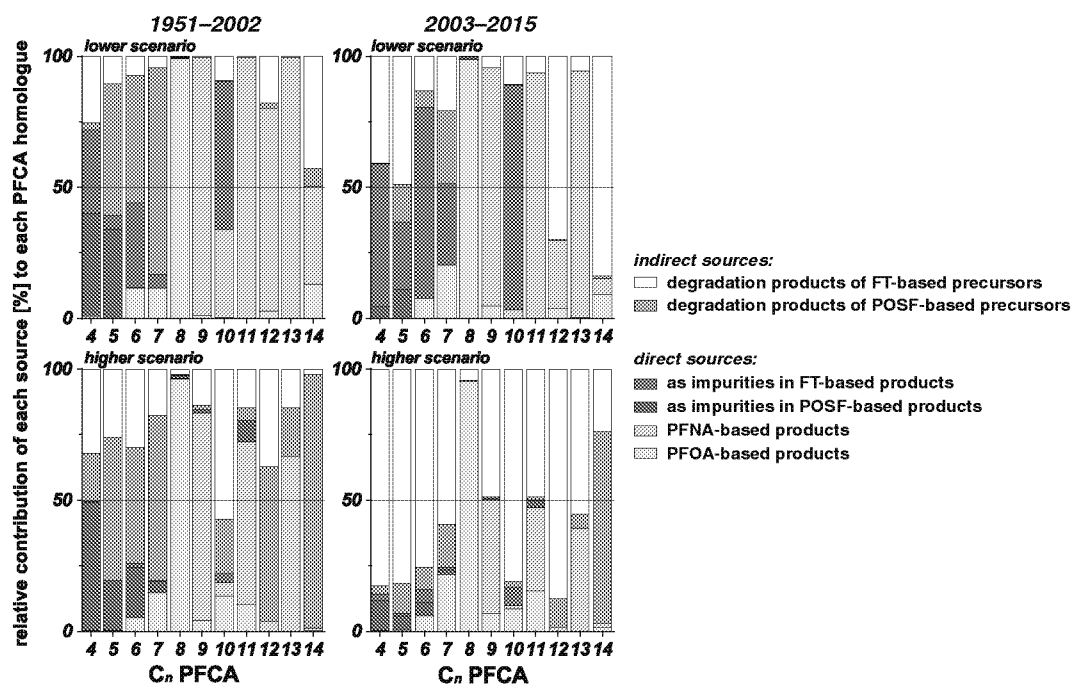


Fig. 5. Relative contributions of each source to estimated total global emissions from all quantified sources for individual C_4 – C_{14} PFCa homologues in 1951–2002 (pre-phase-out) and 2003–2015 (transition after phase-out).

Table 2

Estimated global cumulative emissions of C₄–C₁₄ PFCA homologues (1951–2030) from quantified sources in tonnes. Numbers in brackets indicate the percentage of emissions from direct sources. The percentage of emissions from indirect sources can be calculated as 100% minus these percentages. N.A. – not applicable.

C _n PFCA	1951–2002 [t]		2003–2015 [t]		2016–2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C ₄ PFCA / PFBA	5 (72%)	402 (50%)	5 (58%)	220 (14%)	6 (17%)	293 (3%)	15 (47%)	915 (26%)
C ₅ PFCA / PFPeA	14 (39%)	690 (20%)	5 (37%)	305 (7%)	7 (8%)	382 (2%)	26 (31%)	1377 (12%)
C ₆ PFCA / PFHxA	16 (26%)	1061 (26%)	17 (80%)	513 (16%)	5 (98%)	117 (48%)	39 (59%)	1691 (24%)
C ₇ PFCA / PFHpA	44 (17%)	2123 (19%)	13 (51%)	774 (24%)	2 (94%)	358 (64%)	59 (26%)	3264 (26%)
C ₈ PFCA / PFOA	1344 (100%)	8184 (98%)	730 (100%)	4773 (96%)	3 (100%)	5408 (100%)	2078 (100%)	18366 (98%)
C ₉ PFCA / PFNA	222 (100%)	1371 (85%)	28 (96%)	469 (51%)	0 (0%)	62 (72%)	250 (99%)	1901 (76%)
C ₁₀ PFCA / PFDA	3 (91%)	109 (22%)	4 (89%)	93 (17%)	1 (100%)	20 (66%)	8 (91%)	222 (24%)
C ₁₁ PFCA / PFUnA	59 (99%)	471 (80%)	7 (93%)	173 (50%)	0 (N.A.)	45 (83%)	67 (99%)	689 (73%)
C ₁₂ PFCA / PFDoA	0 (80%)	40 (4%)	0 (0%)	20 (1%)	0 (N.A.)	3 (0%)	0 (63%)	63 (3%)
C ₁₃ PFCA / PFTrA	15 (99%)	109 (67%)	2 (94%)	35 (39%)	0 (N.A.)	3 (0%)	17 (99%)	147 (59%)
C ₁₄ PFCA / PFTeA	0 (0%)	16 (1%)	0 (0%)	2 (0%)	0 (N.A.)	1 (0%)	0 (0%)	19 (1%)

at downstream industrial sites such as textile or paper factories where products containing POSF- or fluorotelomer-based products are used.

A trend in the geographical distribution of major industrial sites is that production of PFCAs, fluoropolymers and other PFAS products

has shifted from Japan, Western Europe and the US to the emerging economies in continental Asia (e.g., China and India), suggesting that the proportion of global PFCA emissions originating from continental Asia has increased. Detailed analyses for each product group (including references) are provided as follows.

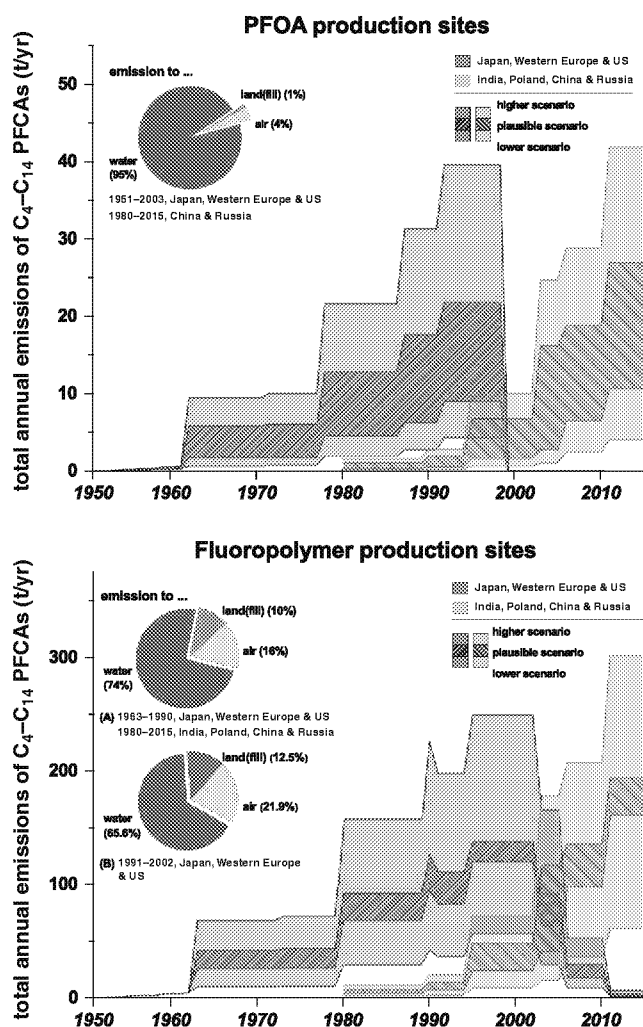


Fig. 6. Estimated annual releases of PFCAs from PFOA production sites (top) and fluoropolymer production sites (bottom) in the United States (US), Western Europe and Japan (purple) as well as in China, Russia, Poland and India (orange). The pie charts show fractions of emissions to different environmental media. The colored areas represent the estimated ranges of annual emissions based on the full ranges of the APFO/NaPFO use rates from patents; the areas shaded in dark represent the estimated ranges of annual releases based on the APFO/NaPFO use rate of 0.3 wt% of relevant fluoropolymers produced (plausible scenario).

i. *PFOA-based products.* There has been a rapid increase in domestic demand and production of PTFE in China since the late 1990s (from 6.6 kt/yr in 1999 to about 64 kt/yr in 2012) (Cai, 2009; Fang, 2004; Kälén et al., 2012; Wang, 2006). Thus, the amounts of PFOA-based products produced in China (initiated in the 1960s in Shanghai; Huang et al., 2010) increased accordingly from a negligible amount before the 1990s to an annual production capacity of about 50–80 tonnes in 2009, with at least five production sites now in China (Mei, 2008). Similarly, PTFE production increased in India after 2010 (ca. 2.3 kt in 2011 and 7.5 kt in 2012; Kälén et al., 2012), resulting in a likely increase in use of PFOA-based products as fluoropolymer processing aids. Thus, releases of PFCAs from these production sites of PFOA-based products and fluoropolymer production sites in China and India have likely increased (Fig. 6, orange areas). In contrast, after 2000, major PFOA producers in Japan, Western Europe and the US subsequently ceased PFOA production (e.g. 3M in 2002 (3M, 2000a); Dyneon in 2004 and Mitani in 2010 (OECD, 2009); Daikin in 2012 (Daikin, 2013); and DuPont in 2013 (DuPont, 2013)), and the remaining production was/is mostly conducted in closed processes with marginal losses only (DuPont, 2005; OECD, 2009; US EPA, 2006). At the same time, major fluoropolymer producers in these regions implemented technologies to recover and reuse PFOA from wastewater streams (3M, 2009; Chapman, 1998; OECD, 2009) and started to use PFOA-free alternatives in the polymerization processes (Dyneon uses alternatives only from 2009 (Dyneon, 2011), Asahi from 2011 (Asahi, 2009 a,b), Daikin and Solvay from 2013 (Daikin, 2013; Solvay, 2013), and DuPont from mid-2013 (DuPont, 2013)). These actions have led to decreasing PFCA releases from production sites in Japan, Western Europe and the US after 2000 (Fig. 6, purple areas). The increase in PFCA emissions at the manufacturing sites of PFOA-based products and fluoropolymers in country group II is likely much faster than the decline at such sites in country group I in the period 2002–2012, causing a re-increase of global annual PFCA emissions as illustrated in Fig. 4. It should be noted that several major Chinese fluoropolymer producers have also developed technologies to recycle PFOA from waste streams (Feng and Su, 2007; Tang et al., 2009) or industrialized production with alternative substances replacing PFOA-based products (Wang et al., 2010; Xie et al., 2011; Xu et al., 2011); however, due to a lack of quantitative data, the corresponding reduction of PFCA releases from these sites in China cannot be quantified and has not been included here. In addition to these industrial activities, regulatory activities have been undertaken in China. In 2011, PFOA-relevant technology and products were added to the *Catalogue for the Guidance of Industrial Structure*

Adjustment (NDRC, 2011), including that new installation of PFOA production facilities shall be restricted and that PFOA-containing paints and fluoropolymers that use PFOA in the polymerization shall be eliminated. In 2013, fluoropolymers that use PFOA in the polymerization were recognized as products with high pollution and high environmental risk (“dual-high” products) in the *Comprehensive Catalog for Environmental Protection* (China MEP, 2013). However, it is currently unclear when the producers in regions such as China, India and Russia will phase-out PFOA-based products, as a detailed timeline for the restriction and elimination of PFOA in these regions is not currently available.

ii. *PFNA-based products*. Reports from the only known producer and major industrial users (i.e., PVDF producers) in Japan, Western Europe and the US show that emissions related to PFNA-based products from their production sites were likely reduced in the last few years (APFN Work Group, 2003) and PFCA-free alternatives have been developed and partially implemented (Arkema, 2011). Although PVDF production in China started to increase rapidly after 2008 (3F, 2011; Kälén et al., 2012), the producers there have likely used either PFOA-based products or PFCA-free alternatives in the polymerization process, but not PFNA-based products (Arkema, 2008; Zhao et al., 2011). Hence, it is likely that emissions from the life-cycle of PFNA-based products have been reduced worldwide since 2002.

iii. *POSF-based products*. The geographical shift has also been observed for the industrial sites that produce and use POSF-based products. After 3M ceased its global production of POSF-based products in 2002, there were still a few producers in Japan and Western Europe: about 50–160 tonnes of POSF-based products were produced in 2003 in Belgium, Germany, Italy and Japan (OECD, 2005); and 73–162 tonnes in 2005 (OECD, 2006). We assumed that production in these regions decreased linearly thereafter and only negligible amounts (for those uses for which exemptions have been defined under the Stockholm Convention) were produced after 2008, due to regulatory efforts under the EU Directive 2006/122/EC and the Stockholm Convention on Persistent Organic Pollutants. Meanwhile, major downstream industrial users in these regions such as hard metal plating started to use alternatives (OECD, 2006; UNEP, 2012; Wang et al., 2013). Hence, there is likely a strong decrease of emissions of PFCA impurities and POSF-based PFCA precursors from these industrial sites in Japan, Western Europe and the US after 2002. In contrast, large-scale production began in China in 2003, with extensive use of polymeric POSF-based products in textile, carpet and leather surface treatments between 2003 and 2008 (in a similar amount to the uses of non-polymeric products) (Zhang et al., 2012). Reported total annual production in China before 2004 was less than 50 t/yr, expanded to about 250 t/yr by 2006, and declined to 100 t/yr in 2008 (China MEP, 2008; Huang et al., 2010; Lim et al., 2011; Zhang et al., 2012). The remaining uses are mainly in metal plating, aqueous film-forming foams (AFFF) synthesis and sulfluramid (insecticide) formulation (Zhang et al., 2012). Recently, Chinese manufacturers have developed or are developing alternative substances to replace PFOS and related chemicals (UNEP, 2012; Wang et al., 2013). Furthermore, POSF-based products have been added by Chinese regulators to China's domestic *Catalogue for the Guidance of Industrial Structure Adjustment* (NDRC, 2011) so that new installations of POSF production facilities shall be restricted and paints containing POSF-based substances shall be eliminated. However, a detailed phase-out plan is not yet available.

iv. *Fluorotelomer-based products*. It is currently unclear how the geographical distribution of emissions from industrial sites where fluorotelomer-based products are manufactured and used change with time (our estimates represent production and emissions on a global scale without regional resolution). Historically, production of fluorotelomer-based products was located in Japan, Western Europe and the US (Banks et al., 1994; Prevedouros et al., 2006). Recently, manufacturers in China also started the production of fluorotelomer-based substances at a minimum of two sites (Fuxin, 2013; Ruan et al., 2010)

and one manufacturer may have initiated production in India (AFT, 2013). Thus, it is likely that emissions of fluorotelomer-based products from industrial sites have increased in China and India. The relative weight of emissions at industrial sites between regions, however, cannot be determined due to scarce information regarding the amounts produced and used in all regions.

4. Discussion

4.1. Comparison to Prevedouros et al. and other literature

Here we focus on the evaluation of our newly estimated emissions that occur during the life-cycle of POSF- and fluorotelomer-based products.

We estimated considerably higher releases of PFCAs as impurities in POSF-based products than Prevedouros et al. (2006) (ca. 5 times in our higher scenario; sources 7 and 8 in Table 1). This higher estimate is caused by the fact that the levels of PFCA impurities (200–1600 ppm) in Prevedouros et al. (2006) represent only the PFOA content in products (3M, 2003), whereas we include impurity levels of all C₄–C₁₄ homologues (400–13300 ppm) based on four recent studies (3M, 2003; Naile et al., 2010; Reagen et al., 2007; Seacat et al., 2003; for details see Section S1.3.2 in the *Supplementary Data*). It is possible that these estimated levels of PFCA impurities are still underestimated because in an early study, a 1% (i.e. 10000 ppm) yield of solely perfluorooctanoyl fluoride impurity (which is the starting material to produce PFOA) formed in the electrochemical fluorination to produce POSF was reported (Gramstad and Haszeldine, 1957). In addition, measurements of PFCAs in a few technical products show that the levels of PFCA impurities vary considerably within a production line and among products (Jackson and Mabury, 2013; Naile et al., 2010; Reagen et al., 2007; Seacat et al., 2003). Hence, further studies on PFCA impurities in POSF-based products are needed to improve the understanding of this historical source. Note that part of the PFCA impurities formed during the production of POSF can react with the substances added in the subsequent reactions of POSF and form derivatives such as perfluorooctanamides (C₇F₁₅CONH(R), R = CH₃ or C₂H₅) and their homologues (Jackson and Mabury, 2013). Similar to their sulfonamide analogues, these perfluoroalkane carboxamides can be transformed back into the corresponding PFCAs (and their shorter-chain homologues) through OH-radical mediated reactions in air (Jackson et al., 2013) and enzymatic hydrolysis in biota (Seacat, 2004) and thus act as sources of PFCAs. Therefore, in addition to C₄–C₁₄ PFCA homologues, their derivatives in technical products (e.g. perfluoroalkane carboxamides, see Jackson and Mabury, 2013; methyl esters, see Hanari et al., 2014) should be considered in future studies. Given that these historical POSF-based products are no longer manufactured, obtaining samples for future studies is problematic.

Two changes made in this study contribute to the higher estimates of PFCAs released from degradation of POSF- and fluorotelomer-based precursors (Table 1, sources 11 and 12). First, in addition to residuals, which were treated as the only source of PFCA precursors in Prevedouros et al. (2006), we take two more sources into account, namely [i] PFCA precursors such as EtFOSAs and FTSAs that are present in products as ingredients, and [ii] substances with complex structures that may break down to PFCA precursors such as EtFOSE or FTOHS. Second, we used updated degradation yields in the calculations that were derived from recent studies showing that a wide range of PFCA homologues can be formed from precursors under varied conditions. For example, N-ethyl perfluorobutane sulfonamide (EtFBSA) may transform into C₂–C₄ PFCAs through OH radical oxidation (Martin et al., 2006), and 8:2 FTOH (C₈F₁₇C₂H₄OH) can degrade into C₆–C₈ PFCAs biotically (Liu et al., 2007; Wang et al., 2005) or C₅–C₉ PFCAs through OH radical oxidation (Ellis et al., 2004). Details on emissions of POSF- and fluorotelomer-based PFCA precursors and degradation yields of

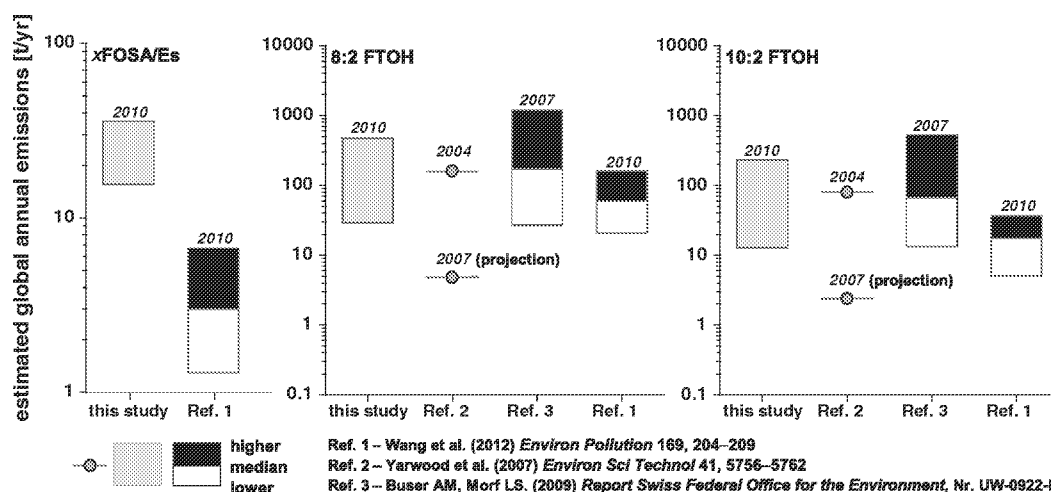


Fig. 7. Estimated emission ranges of xFOSA/Es, 8:2 FTOH and 10:2 FTOH in 2010 in this study (gray boxes) and estimated emission ranges in 2004 and 2007 from Yarwood et al. (2007), in 2007 from Buser and Morf (2009) and in 2010 from Wang et al. (2012) (black/white boxes).

PFCA precursors are provided in Sections S1.3.3 and S1.4.3 in the *Supplementary Data*.

To evaluate our estimates for emissions of POSF- and fluorotelomer-based PFCA precursors, we compared our results for 8:2–14:2 FTOHs as well as perfluorooctane sulfonamides and sulfonamidoethanols (xFOSA/Es, $x = \text{CH}_3$ and C_2H_5) with three studies conducted with different approaches (Buser and Morf, 2009; Müller et al., 2012; Wang et al., 2012; Yarwood et al., 2007) (see Fig. 7 and Table S65 in the *Supplementary Data*). Yarwood et al. (2007) estimated emissions of 8:2–14:2 FTOHs in North America in 2004 and 2007, based on DuPont's sales data and reduction plan, respectively. Using the emission estimates in 2004 as input data, a North America-based air quality model predicted FTOH levels in air that were in agreement with monitoring data, suggesting that the 2004-emission scenario is plausible (Yarwood et al., 2007). Buser and Morf (2009) reported emission estimates for 8:2 and 10:2 FTOHs into air in Switzerland in 2007, based on a substance flow analysis for residual contents of FTOHs detected in samples including aqueous dispersions of fluorotelomer-based polymers and other fluorinated surfactants. Wang et al. (2012) used a multimedia mass-balance model that describes the day-night cycle of (semi-)volatile organic chemicals in air to interpret day-night measurements of FTOHs (8:2 and 10:2) and xFOSAs performed in summer 2010 in Zurich, Switzerland (Müller et al., 2012). They estimated the source strength of these PFCA precursors released during the use and disposal of consumer products from Zurich, where there is no PFAS-related industry. To compare our emission estimates to these other studies, all estimates were normalized to global annual emissions based on per-capita emissions (data are listed in Table S65 in the *Supplementary Data*), since: (i) FTOHs and xFOSA/Es are primarily emitted from use of household consumer products; (ii) uses and levels of FTOHs and xFOSA/Es are broadly similar in households in industrialized regions throughout the industrialized world, as observed in air monitoring studies (Shoeib et al., 2011).

For xFOSA/Es, our emission estimates are ca. 14–29 t/yr higher than the range of xFOSAs emissions in Wang et al. (2012) (Fig. 7, left). This is likely caused by the different scope of these two studies. Estimates in Wang et al. (2012) represent only emissions during the use and disposal of consumer products such as paper, textiles and carpets that were treated with POSF-based products, whereas estimates in the present study also include use of EtFOSA in insecticides in Brazil (ca. 30 t/yr; assuming 50–100% emitted) (UNEP, 2007). Thus, our “bottom-up” estimates of xFOSA/Es emissions are in good agreement with the combined modeling and monitoring studies (Müller et al., 2012; Wang et al., 2012).

For 8:2 and 10:2 FTOHs, the higher bounds of the estimates in the current paper are slightly higher than the median value of the 2004-emission scenario (by less than a factor of 3) and much higher than the median value of the 2007-emission scenario in Yarwood et al. (2007) (Fig. 7, middle and right). This finding is consistent with a monitoring study (Shoeib et al., 2010) reporting that levels of 8:2 FTOH in air samples collected on the Gulf of Mexico and East Coast Carbon Cruise in 2007 are close to the model results of Yarwood et al. (2007) based on the 2004-emission scenario. In addition, our estimated emission ranges are well within the range of emissions estimated by Buser and Morf (2009) and slightly higher (by factors of 3 and 6 for 8:2 and 10:2 FTOH in the higher scenario, respectively) than the emission ranges estimated by Wang et al. (2012). Similarly to xFOSA/Es, emission estimates in Wang et al. (2012) represent solely diffusive releases from use and disposal of consumer products, whereas our estimates also take production and processing by downstream industrial users into account. For 12:2 FTOH, the median value of the 2004-emission scenario in Yarwood et al. (2007) is within the range of our estimates; the median value of 14:2 FTOH from the 2004-emission scenario in Yarwood et al. (2007) is slightly higher than our estimates (see Table S65 in the *Supplementary Data*).

In summary, our improvements on the emission quantification of PFCA precursors (8:2–14:2 FTOHs and xFOSA/Es) are reasonable; but there are still important data gaps, as indicated in the *Uncertainty Analysis* section. The ongoing high emissions of 8:2 and 10:2 FTOHs, instead of a sharp decrease as projected by Yarwood et al. (2007), are likely caused by one or a combination of the following factors: (i) not all fluorotelomer producers and/or downstream industrial users follow a similar emission reduction plan as projected by Yarwood et al. (2007); (ii) despite the reduction of the relative emissions (per kg of products), the absolute emissions have not decreased due to increasing amounts of products being produced and used; (iii) new producers started to manufacture and process fluorotelomer-based products, for example, in China (Fuxin, 2013; Ruan et al., 2010) and India (AFT, 2013); (iv) Yarwood et al. (2007) assumed that emissions occur only in the year when 8:2 and 10:2 FTOHs were produced, thus a lag time of emissions during the use and disposal that occurs in reality was not considered.

4.2. Comparison to estimated ocean inventory

Since ocean water is the major global reservoir of PFOA, PFNA and likely the other PFCA homologues (Cousins et al., 2011), we used an inventory of C_4 – C_{14} PFCA homologues in open ocean surface water (denoted as the “ocean inventory” in the following) derived from

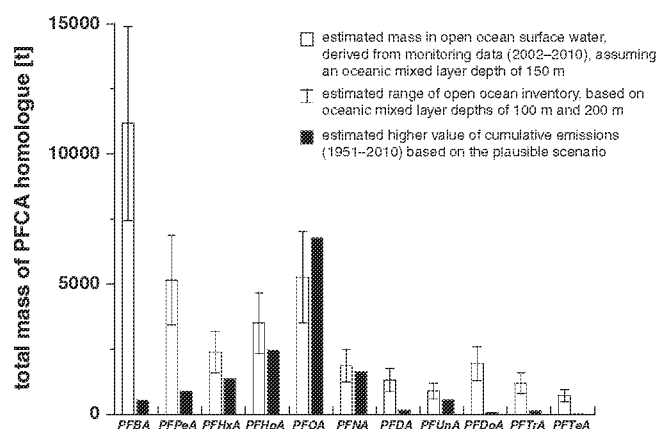


Fig. 8. White: estimated ocean inventories of C_4 – C_{14} PFCAs derived from monitoring studies (Ahrens et al., 2009, 2010; Benskin et al., 2012b,c; Cai et al., 2012a,b; Wei et al., 2007; Yamashita et al., 2005, 2008; Zhao et al., 2012) based on the median oceanic mixed-layer depth of 150 m. Black: higher values of our cumulative emissions of C_4 – C_{14} PFCA homologues until 2010, based on the use rate of 0.3 wt% PFOA-based products as processing aids in fluoropolymer production (i.e. plausible scenario). The error bars represent the range of ocean inventory based on oceanic mixed layer depths from 100 to 200 m).

monitoring studies (Ahrens et al., 2009, 2010; Benskin et al., 2012b,c; Cai et al., 2012a,b; Wei et al., 2007; Yamashita et al., 2005, 2008; Zhao et al., 2012) for another independent evaluation of our results. We have made two changes in estimating the ocean inventory in comparison to Prevedouros et al. (2006): (i) we extended the ocean inventory in the Northern Hemisphere to a global ocean inventory by taking monitoring studies from the Southern Hemisphere into account; (ii) instead of using the range of measured PFCA levels, we used the software “ProUCL 4.1” from US EPA to perform a statistical analysis that includes “non-detect” samples (i.e. those that are measured above the detection limit, but below the quantification limit) to calculate the 95% upper confidence limit of the background level. For details on raw data and data analysis, see Section S2.5 in the *Supplementary Data*. The comparison of our estimated emissions and the ocean inventory is shown in Fig. 8.

The higher values of our emission inventories of C_7 – C_9 and C_{11} PFCAs show a good agreement with the ocean inventories based on the median oceanic mixed layer depth (150 m); they are within or close to a factor of 1.5. This indicates that the major sources of these PFCA homologues have been covered in this study (see also Fig. 5 and Table 2). For the other PFCA homologues, particularly C_4 , C_5 , C_{10} , C_{12} – C_{14} PFCAs, the ocean inventory substantially exceeds our emission inventory and there thus appear to be missing sources.

Despite the large uncertainty associated with the ocean inventory caused by limited measurements (in the case of C_4 and C_5 PFCAs, about 80% of measurements are “non-detect” samples; Ahrens et al., 2010; Cai et al., 2012a,b), the substantial discrepancy between the ocean inventory and the emission inventory for the C_4 , C_5 , C_{10} , C_{12} – C_{14} PFCAs could have the following plausible explanations. First, the newly identified but currently unquantifiable sources shown in Fig. 2 may have contributed significantly to the presence of these PFCA homologues in the environment. For example, PFCAs may be emitted as ingredients, impurities and/or degradation products during the life-cycle of C_4 – C_7 PFCA- as well as C_4 – C_7 and C_{10} PASF-based products that were already in use in the US in the 1980s or even earlier (>4.5 t/yr) (US EPA, 2013b). In addition, some other commercially available substances such as hydrofluoroethers (HFEs) or odd-carbon-numbered fluorotelomer alcohol ($n:1$ FTOH or $CF_3(CF_2CF_2)_nCH_2OH$, $n = 1$ or 2) may undergo atmospheric transformation and form short-chain PFCAs (Bravo et al., 2010). Details on these new sources are presented in the companion paper (Wang et al., 2014). Second, the levels of PFCA

homologues as impurities in POSF- and fluorotelomer-based products may have been underestimated, since they are derived from very limited measurements (see Sections S1.3.2 and S1.4.2 in the *Supplementary Data*). Third, emissions of long-chain fluorotelomer-based precursors (e.g. 14:2 FTOH) may have been underestimated.

4.3. Uncertainty analysis

In Tables S66 to S68 in the *Supplementary Data*, we provide for all parameters: their origin (including references and whether they were estimated or assumed), estimated uncertainty level indicated by uncertainty score, and location of further details to be found in the *Supplementary Data*. In general, the uncertainty levels increase in the order: [i] PFOA-based products \leq PFNA-based products $<$ POSF-based products $<$ fluorotelomer-based products; [ii] production phase $<$ use and disposal phase; [iii] emissions from 1951 to 2015 $<$ emissions from 2016 to 2030.

For PFOA-based products, the estimated amounts used in fluoropolymer production have the largest uncertainty, due to: [i] the use rates are reported with wide ranges; and [ii] the transition process to non-PFCA alternatives after 2002 has only been roughly reported. To address the first uncertainty, we propose a plausible scenario that is likely to be close to actual industrial practice; regarding the second uncertainty, we may overestimate the amounts used in recent years, which can only be corrected with new information. For PFNA-based products, the composition of PFCA homologues in products is the most uncertain parameter, since only one measurement is available. For POSF- and fluorotelomer-based products, only little information is available for the use and disposal phase, due to the huge diversity of products involved, leading to wide ranges of emissions estimated in this study. In addition, the estimated production of fluorotelomer-based products is highly uncertain.

Furthermore, the projections of PFCA emissions (2016–2030) have much higher uncertainties in comparison to the emission estimates for the period before 2016, due to the large uncertainty associated with the elimination of production and use of long-chain PFASs in country group II. There is evidence that action is being taken in these regions to replace long-chain PFASs with alternative substances (for references, see Section 3.3, *Analysis of industrial sources*, and Wang et al., 2013); therefore, the production, use and emissions of long-chain PFASs are likely being reduced in these regions. However, a quantitative emission reduction strategy has not currently been reported for these regions.

5. Future prospects

In this review we have for the first time provided homologue-specific global emission estimates for C_4 – C_{14} PFCAs from 1951 to 2030. Quantified sources of PFCAs include PFOA-, PFNA-, POSF- and fluorotelomer-based products (see Fig. 2). The dominant sources differ (in some cases considerably) between individual PFCA homologues and the relative contributions of different sources change over time. The emission estimates are possibly too low for some homologues (especially C_4 and C_5 PFCAs) because there are newly identified but currently unquantifiable sources, including (i) historical and current use of products based on C_4 – C_7 perfluoroalkane carbonyl fluorides (PACFs) as well as C_4 – C_7 and C_{10} PASFs and (ii) potential formation from fluoropolymers, side-chain fluorinated polymers or other unknown precursors (for details on these currently unquantifiable sources, see companion paper; Wang et al., 2014).

Our emission estimates are global totals and thus the PFCA homologue pattern in the inventories may differ from those observed in environmental and biota samples taken at specific sites because (i) environmental and biota samples reflect the influence of various local sources, and (ii) the PFCA homologue source pattern can be significantly transformed between emission and samples taken in environmental or

biological media due to differences in the fate and bioaccumulation of individual homologues. Nevertheless, our emission inventory is a further step towards the goal of understanding the variability in PFCA homologue patterns in environmental and biological matrices in different geographical regions. We encourage environmental fate studies to take advantage of the data presented here, particularly in continental Asia where future emissions will predominantly occur.

Conflict of Interest

R.C. Buck is an employee of E.I. duPont de Nemours and Company, Inc., a global manufacturer of fluoropolymers and fluorotelomer-based products.

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Appendix A. Supplementary data

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